THE VELOCITY OF SPLITTING OFF OF CHLORINE FROM MONOCHLORACETATE.

By Sinnosuke MATUURA.

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When monochloracetic acid is acted on by water, it is partially converted into glycolic acid and hydrochloric acid, according to the equation

$$CH_2ClCOOH + H_2O = CH_2OHCOOH + HCl.$$

The velocity of this decomposition or hydrolysis is very slow, but that of the salt is rapid and especially accelerated by the presence of alkalies in excess.

Many investigations on this subject have been carried out. Buchanan[1] made a study of the velocity of decomposition by heating the solution of monochloracetate. Lossen and Eihoff[2] measured the velocity of decomposition at room temperature. After keeping the solution for 500 days, the quantity of decomposed product was determined. Euler[3] repeated Schwab's[4] experiment on the velocity of decomposition of monochloracetate by the presence of sodium hydroxide at 65 and 80°C. Senter[5] investigated the velocities of decomposition of monochloracetic acid and its salts, with or without caustic soda at 74.4 and 102°C. Johanson[6] measured the velocity of reaction of the barium salt with barium hydroxide, and of the sodium salt with sodium hydroxide respectively at 250°C. But their concentration of the solution was determined after a long interval from the start of reaction. Drushel and Simpson[7] also measured the velocity of decomposition of sodium monochloracetate at 70 and 90°C. Euler and Fahlander[8] investigated the velocity of decomposition of sodium monochloracetate with sodium hydroxide or with other catalysers. Hedelius[9] determined the velocity of splitting off of chlorine from monochloracetate, acting with sodium hydroxide at 55–90°C.

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(1) *Ber.*, **4** (1971), 340, 863.
(2) *Ann.*, **342** (1905), 116.
(3) *Ber.*, **39** (1906), 2726.
(4) *Etudes Dyn. chem.* 1884, 20.
(5) *Z. physik. Chem.*, **70** (1910), 511.
(6) *Z. physik. Chem.*, **79** (1912), 621.
(7) *J. Am. Chem. Soc.*, **39** (1917), 2456.
(8) *Z. physik. Chem.*, **100** (1922), 171.
(9) *Z. physik. Chem.*, **96** (1920), 343.

Thus many papers are published on this subject, yet in none of them can be found the determination of the course of reaction in earlier stage at lower temperature.

The author has made a research on the velocity of the reaction within about 3 hours with or without caustic alkali at 25–35°C. The results obtained are reported below.

Theoretical.

As above mentioned, monochloracetate is decomposed in aqueous solution with caustic alkali as the following:—

$$CH_2ClCOOK+KOH = CH_2OHCOOK+KCl$$

Assuming that a represents the initial concentration (in mols) of monochloracetate, b that of caustic alkali and x the decomposed amount of monochloracetate (or produced chloride) at the end of time t, the velocity of the reaction can be expressed by

$$\frac{dx}{dt} = k(a-x)(b-x) ,$$

k being the constant of velocity.

In case $a \neq b$, on integration, we obtain the expression

$$\frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt ,$$

or

$$e^{(a-b)kt} = \frac{b(a-x)}{a(b-x)} .$$

As x and kt are small and the high powers of $\frac{x}{a}$ and $\frac{x}{b}$ can be neglected, we may write

$$1+(a-b)kt = \left(1-\frac{x}{a}\right)\left(1+\frac{x}{b}\right) .$$

then

$$1+(a-b)kt = 1-\frac{x}{a}+\frac{x}{b} .$$

Hence

$$k = \frac{x}{abt}$$

In case $a = b$, the equation becomes

$$\frac{dx}{dt} = k(a-x)^2 ,$$

which gives, on integration,

$$\frac{1}{a-x} - \frac{1}{a} = kt ,$$

or

$$\frac{x}{a\,a-x)} = kt .$$

As x is small, we may write

$$k = \frac{x}{a^2 t} .$$

In either case, the decomposed quantity of monochloracetate (or produced chloride) is proportional to the product of concentrations of both monochloracetate and caustic alkali at their initial state and the time. If monochloracetate has been decomposed partially at initial state, we must write $x = \alpha + \beta t$ instead of $x = kabt$, where α represents the decomposed monochloracetate at initial state and $\beta = k\,a\,b$.

In the case where only monochloracetate exists in the solution, the reaction may be as follows:—

$$CH_2ClCOOK + H_2O = CH_2OHCOOH + KCl.$$

As the reaction proceeds, the acidity of the solution increases. This reaction to some extent may be considered as monomolecular. Hence the velocity of the reaction can be expressed as follows:—

$$\frac{dx}{dt} = k(a-x)$$

where a is the concentration of monochloracetate at initial state, and x the decomposed quantity of this salt at time t. On integration, we have

$$\ln \frac{a}{a-x} = kt .$$

As x and kt are small, we may write

$$k = \frac{x}{at} .$$

Similarly as described above, in case monochloracetate has been decomposed partially at first, we may write $x = a + \beta t$ instead of $x = kat$, where $\beta = ka$.

If we measure the concentration of produced chloride and the time, we can calculate the velocity constant of the reaction.

Experimental.

The experiment is carried out as follows. The solutions of monochloracetic acid and caustic alkali are kept in a thermostat, and mixing the two solutions, a portion of the solution is drawn out at a certain time and a silver nitrate solution is added both to this sample acidified with nitric acid and to the standard solution of potassium chloride. The two solutions are compared by using the nephelometer of Clet Co.

The chemicals used are obtained from Kahlbaum. The results of the experiments are shown in Tables 1, 2 and 3.

Table 1.

$CH_2ClCOOK + KOH$

Exp. No.	Temp. C.	Initial state (M.)	$\beta \times 10^4$	t. min.	$x \times 10^4$(M.) obs.	$x \times 10^4$(M.) calc.
1	20	$a = 0.3113$ $b = 0.2965$	0.02092	30 60 91 125 150 180 210 240 270	3.30 3.82 4.45 4.94 5.95 6.61 7.05 7.53 8.19	3.24 3.87 4.51 5.23 5.75 6.38 7.00 7.63 8.26
2	25	$a = 0.3000$ $b = 0.3000$	0.04195	20 40 60 90 150 180 210	2.68 3.42 3.89 5.30 8.08 9.59 10.20	2.51 3.35 4.19 5.45 7.96 9.22 10.48
3	25	$a = 0.3084$ $b = 0.4077$	0.07230	30 60 90 120 150 180	4.61 6.85 8.35 10.65 13.02 15.63	4.43 6.60 8.77 10.94 13.10 15.27

Table 1.—(*Concluded*)

Exp. No.	Temp. C.	Initial state (M.)	$\beta\times10^4$	t. min.	$x\times10^4$(M.) obs.	$x\times10^4$(M.) calc.
4	30	$a = 0.3000$ $b = 0.3000$	0.12117	40	4.54	3.79
				60	6.85	6.22
				90	8.46	9.85
				120	13.04	13.49
				150	17.44	17.12
				180	19.63	20.76
				210	25.66	24.39
5	30	$a = 0.4000$ $b = 0.3000$	0.13593	30	4.50	4.20
				45	6.16	6.24
				60	7 37	8.28
				90	12.73	12.36
				120	16.69	16.44
				150	19.24	20.52
				180	28.15	24.59
				210	26.47	28.67
6	30	$a = 0.4000$ $b = 0.4000$	0.20095	40	7.76	5.84
				60	10.00	9.85
				90	15.31	15.88
				120	21.44	21.91
				150	22.52	27.94
				180	36.88	33.97
				210	41.48	40.00
7	30	$a = 0.5000$ $b = 0.5000$	0.29491	40	14.65	15.18
				60	21.62	21.08
				90	30.26	29.93
				120	38.43	38.77
8	30	$a = 0.3000$ $b = 0.3000$ $KNO_3 = 0.5000$	0.07226	12	2.73	2.72
				25	3.47	3.66
				40	4.85	4.74
				60	6.13	6.19
				90	8.47	8 35
				120	10.38	10.52
				150	13.35	12.69
				180	14.20	14.86
				210	17.16	17.02

Table 2.

$CH_2ClCOONa+NaOH$

Exp. No.	Temp. C.	Initial state (M.)	$\beta\times10^4$	t. min.	$x\times10^4$(M.) obs.	$x\times10^4$(M.) calc.
9	25	$a=0.3000$ $b=0.3000$	0.034472	10 20 40 60 90 120 150 180	1.08 1.36 2.07 2.58 3.87 5.28 5.93 6.65	1.07 1.42 2.11 2.80 3.83 4.86 5.90 6.93
10	30	$a=0.3000$ $b=0.3000$	0.063324	30 60 90 120 180	2.59 4.03 6.09 7.17 12.19	2.23 4.13 6.03 7.93 11.73
11	35	$a=0.3000$ $b=0.3000$	0.19602	10 30 60 90 120 150	1.90 4.72 7.95 18.32 24.49 27.05	1.00 4.92 10.80 16.68 22.57 28.45

Table 3.

$CH_2ClCOOK+H_2O$

Exp. No.	Temp. C.	Initial state (M.)	$\beta\times10^4$	t. min.	$x\times10^4$(M.) obs.	$x\times10^4$(M.) calc.
12	25	0.3000	0.002512	20 60 90 120 150 180 210	1.62 1.84 1.88 2.02 2.07 2.00 2.17	1.69 1.80 1.87 1.95 2.02 2.10 2.17
13	30	0.5000	0.01849	30 45 60 80	1.74 1.86 2.22 2.63	1.67 1.95 2.23 2.60
14	30	0.5000	0.01361	10 25 40 70	1.64 1.70 1.86 2.43	1.56 1.76 1.96 2.37

β is calculated by the method of least squares and then k is obtained from $\beta = kab$ or $\beta = ka$.

In experiment No. 8, beside the reacting substances, potassium nitrate was added; it is shown that the reaction velocity is retarded by the presence of another salt with a common ion.

Tables 4 and 5 give the resumes of the values at each temperature. The results of calculation show a fair agreement with the theory which we assumed at first.

Table 4.

Exp. No.	Temp. C.	Initial conc. (M) $CH_2ClCOOK$	Initial conc. (M) KOH	$\beta\times10^4$	$k\times10^4$	mean
1	20	0.3113	0.2965	0.02092	0.227	
2	25	0.3000	0.3000	0.04195	0.466	0.521
3	,,	0.3084	0.4077	0.07230	0.575	
4	30	0.3000	0.3000	0.12117	1.35	
5	,,	0.4000	0.4000	0.13593	1.13	1.23
6	,,	0.4000	0.4000	0.20095	1.26	
7	,,	0.5000	0.5000	0.29491	1.18	
8	,,	0.3000	0.3000 $KNO_3 = 0.5000$	0.07226		
Exp. No.	Temp.	CH_2COONa	NaOH	$\beta\times10^4$	$k\times10^4$	
9	25	0.3000	0.3000	0.034472	0.381	
10	30	0.3000	0.3000	0.063324	0.704	
11	35	0.3000	0.3000	0.196020	2.18	

Table 5.

Exp. No.	Temp. C	Initial conc. (M.) $CH_2ClCOOK$	$\beta\times10^4$	$k\times10^6$	mean
12	25	0.3000	0.002512	0.8372	
13	30	0.5000	0.01849	3.698	3.21
14	30	0.5000	0.01361	2.72	

In conclusion the author expresses his thanks to Mr. Sigeru Kondô for his assistance.

Summary.

1. Assumed as monomolecular reaction, the velocity of the decomposition of potassium monochloracetate in aqueous solutions is measured,

$$k_{25°} = 0.837 \times 10^{-6} \text{ and } k_{30°} = 3.21 \times 10^{-6}$$

2. The velocities of the following reactions are measured,

$$CH_2ClCOOK + KOH = CH_2OHCOOK + KCl$$
$$k_{20°} = 0.227 \times 10^{-4},\ k_{25°} = 0.521 \times 10^{-4} \text{ and } k_{20°} = 1.23 \times 10^{-4}$$

$$CH_2ClCOONa + NaOH = CH_2OHCOONa + NaCl$$
$$k_{25°} = 0.381 \times 10^{-4},\ k_{30°} = 0.704 \times 10^{-4} \text{ and } k_{35°} = 2.18 \times 10^{-4}$$

The velocity constant of potassium salt is larger than that of sodium salt.

3. The reaction velocity of potassium monochloracetate with potassium hydroxide is retarded by the presence of another salt (i.e. KNO_3).

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ZUR THEORETISCHEN DEUTUNG DER FREUNDLICHSCHEN ADSORPTIONSISOTHERME.

Von Bun-ichi TAMAMUSHI.

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Es sind bisher manche Versuche,[1] die Freundlichsche Adsorptionsisotherme:

$$a = ac^{\frac{1}{n}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

theoretisch zu erklären. Einige von denen hatten Erfolg, obwohl sie noch nicht vollkommen befriedigend zu sein scheinen. Henry[2] hat diese Isotherme aus der Gibbsschen Gleichung abgeleitet, wobei er die Änderung

(1) *J. Phys. Chem.*, **31** (1927), 251 Dort eine Übersicht.
(2) *Phil. Mag.*, 6, **44** (1922), 689.

der freien Oberflächenenergie des Adsorbens durch die monomolekular adsorbierten Moleküle in Betracht gezogen hat. Nach ihm, bedeutet der Exponent $\frac{1}{n}$ das Verhältnis von der osmotischen Arbeit zur gesamten Arbeit bei der Adsorption von a Mol Adsorptivs. Später hat Bancroft[3] eine analoge, aber noch einfachere Herleitung dieser Isotherme angegeben. Die Herleitung solcher Art, die allerdings berechtigt angesehen werden kann, soll im folgenden noch anderweitig und zwar deutlicher ausgeführt werden, indem man hierbei für die adsorbierte Phase zweidimensionale Zustandsgleichung anwendet.

Die folgenden Betrachtungen beziehen sich auf die Grenzfläche fest-gasförmig, wo die Erscheinungen molekularkinetisch verhältnismässig leicht begreifbar sind. Die Anwendung der Gibbsschen Gleichung sowie der zweidimensionalen Zustandsgleichungen zur Grenzfläche fest-gasförmig soll aus jetzt vielfach erkannten Gründen erlaubt werden.

Man nimmt für die adsorbierte Schicht folgende Zustandsgleichung an:

$$(\sigma_0-\sigma)\frac{1}{a} = iRT, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

worin σ_0 die Oberflächenspannung des reinen Lösungsmittels, σ die Oberflächenspannung der Lösung, a die adsorbierte Menge in Mol pro cm^2 der Oberfläche, R die Gaskonstante, T die absolute Temperatur, und i eine Konstante, deren physikalische Deutung bald angegeben wird, bedeutet. Aus dieser Gleichung und der Gibbsschen Gleichung, nämlich:

$$a = -\frac{c}{RT}\frac{\partial\sigma}{\partial c} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

folgt eine Beziehung zwischen a und c (die Konzentration im homogenen Raum):

$$a = kc^{\frac{1}{i}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

worin k eine Integrationskonstante bedeutet. Diese letzte Beziehung stimmt formal mit der empirisch angestellten Adsorptionsisotherme (1) überein.

Es wird nun dem Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ seine physikalische Deutung angegeben. Man hat zuerst[4] den Koeffizient i etwa versuchsweise in

(3) *J. Phys. Chem.*, **31** (1927), 1501.

(4) Tamamushi, Dieses Bulletin, **1** (1926), 185.

Gleichung (2) eingeführt, der sich aber eigentlich auf der Abweichung des Zustandes der adsorbierten Schicht von dem Zustande idealer Schicht beziehen soll. Diese Abweichung hat den Grund im allgemeinen in zwei Faktoren, nämlich, die Flächenbedürfnisse der adsorbierten Moleküle einerseits und die Molekularkräfte zwischen den adsorbierten Moleküle anderseits. Man kann also in diesem Sinne eine andere Zustandsgleichung aufstellen, die inhaltlich mit Gleichung (2) identisch sein soll, und die in Analogie zu der van der Waalsschen Zustandsgleichung der Gase lautet:[5]

$$\left(\pi+\frac{\alpha}{\Omega^2}\right)(\Omega-\beta)=RT\,, \quad \ldots\ldots\ldots\ldots\ldots (5)$$

worin π (gleich $\sigma_0-\sigma$) den Flächendruck, Ω (gleich $\frac{1}{a}$) die Oberfläche in cm^2 pro Mol des adsorbierten Stoffes, β das Flächenbedürfnis der adsorbierten Moleküle pro Mol und α eine Konstante, die sich auf Molekularkräfte bezieht, bedeutet.

Vergleicht man Gleichung (5) mit Gleichung (2), so bekommt man für den Koeffizient i folgenden Ausdruck:

$$i=1+\frac{\beta}{\Omega}-\frac{\alpha}{RT\Omega}\,, \quad \ldots\ldots\ldots\ldots\ldots (6)$$

indem man dabei den höheren Glied $\frac{\alpha\beta}{\Omega^2}$ vernachlässigt.

Der Exponent $\frac{1}{i}$ ist somit abhängig von $\Omega\left(\frac{1}{a}\right)$ bzw. von der Dichte des Adsorptivs im homogenen Raum. Dieser Anspruch spricht aber der Erfahrung nicht wider, denn auch der Exponent $\frac{1}{n}$ in der Freundlichschen Isotherme von Dichte nicht streng unabhängig ist.[6]

Für kleine Dichten, soweit β sowie α vernachlässigt werden können, wird i annähernd gleich 1 sein. Dementsprechend bekommt man aus der Zustandsgleichung der idealen Schicht:

$$\pi\Omega=RT \quad \ldots\ldots\ldots\ldots\ldots (7)$$

und der Gibbschen Gleichung folgende Beziehung

$$a=kc\,, \quad \ldots\ldots\ldots\ldots\ldots (8)$$

die den Henryschen Satz darstellt und die für genügend kleine Dichten auch empirisch bestätigt worden ist.

(5) Vgl. Magnus, *Z. anorg. u. allg. Chem.*, **158** (1926), 67.
(6) Vgl. Freundlich, „Kapillarchemie" Bd. 1 (1930), 157.

Für grössere Dichten, hat man den Einfluss sowohl von β auch von α zu berücksichtigen. Der erste Einfluss wirkt immer derart, dass es den Wert von i grösser als 1 zu machen, aber der zweite wirkt verschieden, je nachdem α positiv oder negativ ausfällt. Die Zwischenmolekularkräfte könnten im Falle der adsorbierten Phase entweder anziehend oder abstossend sein, während sie sich im Falle der Gase stets anziehend wirkt.

Denkt man die Dipolmolegüle, deren elektrischer Dipol asymmetrisch im Molekül liegt, so werden sie an der Grenzfläche so orientiert, dass sie nicht nur miteinander parallel, sondern auch alle gleichgerichtet sind. Es ist klar, dass die Moleküle bei einer solchen Orientierung sich gegenseitig abstossen werden.[7] In diesem Falle kommt i ohneweiteres grösser als 1 aus, da α negativ ausfällt.

Wenn aber die Orientierung der Moleküle an der Grenzfläche eine solche ist, dass sie zwischen ihnen ein Anziehungspotential bedingt, d. h. wenn der Wert von α positiv ausfällt, so wird i entweder grösser oder kleiner als 1 sein, je nachdem

$$\beta - \frac{\alpha}{RT} > 0 , \qquad \text{oder} \qquad \beta - \frac{\alpha}{RT} < 0 .$$

Bei mittleren oder hohen Temperaturen, dürfte im allgemeinen die erste Bedingung erfüllt werden und zwar stehen unsere meisten Beobachtungen (an der Grenzfläche fést-gasförmig) mit dieser Bedingung im Einklang. Erst bei genügend tiefen Temperaturen würde es folgen, dass der Einfluss der anziehenden Kräfte denjenigen der Raumversperrung übersteigt und somit die zweite Bedingung erfüllt wird. Die Realität solcher Verhältnisse müsste noch in bezug auf den „kritischen Zustand der adsorbierten Schicht" diskutiert werden.[8] Wenn aber, jedenfalls, solche Verhältnisse existierten, so müsste sich dies im Verlauf der Adsorptionsisotherme in der Weise äussern, dass sie bei grösseren Dichten nach der Dichte-Achse konvex sein werden, während sie anfänglich konkav nach dieser Achse oder eventuell linear verlaufen.

(7) Eine Abstossungskraft solcher Art ist von Magnus (loc. cit.) für Kohlendioxyd an Kohle angenommen worden.

(8) Hückel, „Adsorption u. Kapillarkondensation" (1928), 195.

Nach der Potentialtheorie von Polanyi[9] könnte solcher Verlauf, der zur Kondensationserscheinung entspricht, schon im Gebiete der mittleren Dichten realisiert werden. Ein einziger solcher Fall (Adsorption von Schwefeldioxyd an technischer Kohle) ist von Polanyi und Welcke[10] beobachtet worden.

In meisten Fällen, ist es aber sehr wahrscheinlich, dass an der Grenzfläche fest- gasförmig der Einfluss der Raumversperrung denjenigen der anziehenden Kräfte übersteigt, denn die stärkeren aktiven Stellen der Oberfläche stufenweise abgesättigt werden. Es wird dann aus Gleichung (6) folgen, dass der Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ kleiner als 1 ausfällt.

Diese Folgerung ist aber natürlich kein Beweis für die Erfahrungen, sondern etwa ein Vorbild, in dem man den wirklichen Verlauf der Adsorptionsisotherme einsehen könnte.

In Fällen, wo die aktiven Stellen der Oberfläche miteinander so weit entfernt sind, dass die Zwischenmolekularkräfte vernachlässigt werden, stellt man eine Zustandsgleichung auf, die lautet

$$\pi(\Omega-\beta) = RT\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Aus dieser Gleichung und der Gibbsschen Gleichung wird die bekannte Isotherme von Langmuir:[11]

$$c = \frac{Ka}{1-\beta a} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

hergeleitet, worin K eine Integrationskonstante bedeutet.

Man sieht weiter, dass sich der Exponent $\frac{1}{i}$ bzw. $\frac{1}{n}$ bei genügend hohen Temperaturen, wo sowohl β auch a vernachlässigt werden können, gegen 1 annähert. Solche Verhältnisse sind auch empirisch erkannt worden.[12]

In bezug auf die Konstante k in Gleichung (4) bzw. a in der Freundlichschen Isotherme (1) wird hier nur kurz bemerkt, dass sie analog wie die Konstante K in der Langmuirschen Isotherme (10) statistisch berechnet werden könnte,[13] denn die beiden Isothermen aus der Gibbsschen

(9) *Verh. Deutsch. physik. Ges.*, **18** (1916), 55; *Trans. Faraday Soc.*, **28** (1932), 330.

(10) *Z. physik. Chem.*, **132** (1928), 321.

(11) Volmer, *Z. physik. Chem.*, **115** (1925), 253; auch Tamamushi, loc. cit.

(12) Vgl. Freundlich, loc. cit. s. 159.

(13) Kar, *Physik. Z.*, **26** (1925), 614.

Gleichung in ganz analoger Weise hergeleitet wurden und die beiden Konstanten k und K dabei eine Integrationskonstante bedeuteten.

Die Überlegungen, die oben angegeben worden sind, nehmen keine Rücksicht auf die Wirkung der in der ersten Schicht adsorbierten Moleküle auf die weiter von der Oberfläche entfernten. Es musste auch dabei abgesehen werden in Fällen, wo es sich um Kapillarkondensation handelt, wo der Verlauf der Isotherme ganz in anderer Weise zu deuten ist.

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STUDIES ON AMINO-ACIDS AND RELATED COMPOUNDS. PART I. ELECTROLYTIC OXIDATION OF GLUTAMIC ACID.

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Although the mechanism of the oxidative decomposition of some natural amino-acids has been studied to some extent by several investigators,[1] yet we have no satisfactory results in this line. The works published are still imcomplete when viewed from the standpoint of organic chemistry, especially electro-organic chemistry.

With regards to the electrolytic oxidation of amino-acids, C. Neuberg[2] has observed that amino-acids lose ammonia, and are converted into aldehydes with an atom of carbon less, when their dilute aqueous solutions are subjected to electrolysis with platinum electrodes.

Fr. Fichter[3] and his collaborators pointed out that glycine and its allies undergo similar electrolytic oxidation, and their mechanisms are expressed by the following equations, glycine being taken as the type.

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(1) H. D. Dakin, *J. Biol. Chem.*, **1** (1905), 171; **4** (1908), 63; *Biochem. J.*, **10** (1916), 319. K. Langheld, *Ber.*, **42** (1909), 2360. W. Denis, *J. Biol. Chem.*, **9** (1911), 365; **10** (1911), 73. H. Wieland u. E. Bergel, *Ann.*, **439** (1924), 196.

(2) C. Neuberg, *Biochem. Z.*, **17** (1909), 270; **24** (1910), 152.

(3) Fr. Fichter u. M. Schmid, *Helv. Chim. Acta*, **3** (1920), 704; Fr. Fichter u. F. Kuehn, *Helv. Chim. Acta*, **7** (1924), 167.

1) $NH_2CH_2COOH + O + 2F = NH_3 + CH_2O + CO_2$ (Initial reaction)

2) $NH_2CH_2COOH + 3O + 6F = NH_3 + 2CO_2 + H_2O$ (Final stage)

They also mentioned that the electrolytic oxidation of amino-acids may be fairly compared with the oxidative de-amination which these compounds undergo in the living organism, but is far more vigorous and profound.

Though the electrolytic oxidation of other amino-acids would be more complicated than the case above mentioned, the elucidation of the mechanism of these reactions would contribute not only to electro-organic chemistry, but also to biochemistry. From this point of view, a series of researches was instituted, and glutamic acid was selected as the first compound for investigation.

Concerning the oxidation of glutamic acid, several papers have been published. E. Ehrlich[4] observed that glutamic acid produced succinic acid by alcoholic fermentation. H. D. Dakin[5] found that succinic acid was a reaction product when glutamic acid was oxidised with hydrogen peroxide. U. Suzuki and Y. Matsuyama[6] oxidised glutamic acid with nitric acid in the presence of vanadic acid and obtained succinic acid. But no adequate investigation has been reported on the electrolytic oxidation of this amino-acid.

The author has first examined the influence of anode material, current density, and diaphragm on the rate of oxidation of glutamic acid. When the anodic oxidation was carried out in an undivided cell under the same conditions, it was found that lead peroxide gave best current efficiency (considered from the yield of ammonia), out of the three kinds of anode materials, namely, carbon, platinum, and lead peroxide, as the following figures show.

Ammonia-Nitrogen to Total-Nitrogen

Pt: 3.9% C: 4.7% PbO_2: 48.5%.

With regards to current density, 2 amp./dm^2. was found to be most favorable for the formation of both ammonia and succinic acid, and no remarkable difference of the nitrogen distribution was found between the experiments in cells with and without diaphragm.

The Oxidation Products.—*d*-Glutamic acid in N.-sulphuric acid was oxidised at a lead peroxide anode with a current density of 2 amp./dm^2. The oxidised solution was subjected to steam distillation and acetic acid

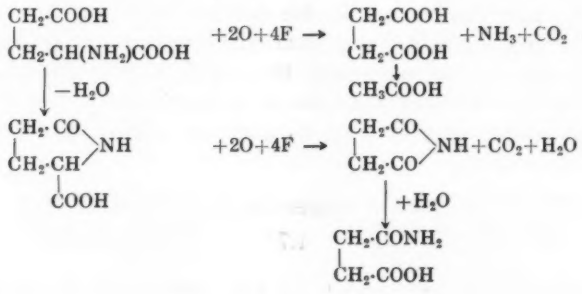
(4) E. Ehrlich, *Biochem. Z.*, **18** (1909), 391.
(5) H. D. Dakin, *J. Biol. Chem.*, **5** (1909), 409.
(6) Japanese patent No. 39210.

was obtained from the distillate. Large quantities of ammonium chloride and of succinic acid as well as unchanged glutamic acid were isolated from the residue of the steam treatments.

From the results of the nitrogen distribution in the solution, it seemed that the presence of some imino or amide compound might be possible. In fact, a small quantity of such a compound was isolated and identified as succinamic acid by comparison with the synthetic sample. The presence of this substance may be considered as derived from pyrrolidone-carboxylic acid. The latter acid was first formed from glutamic acid, then it was oxidised to succinimide, which on partial hydrolysis yielded succinamic acid. The formation[7] of pyrrolidone-carboxylic acid in the solution of glutamic acid is quite probable, and it will be discussed fully in the next paper.

Acetic acid obtained from the electrolysate of glutamic acid was speculated as secondary oxidation product of succinic acid. This has been actually proved by the anodic oxidation of pure succinic acid.

Mechanism of the Reaction. The products obtained from glutamic acid in the above oxidation comprise succinic acid, acetic acid, succinamic acid, ammonia and carbon dioxide. Considering the isolation of these substances as the basis, the course of the oxidation can be explained to be as follows:



Experimental Part.

d-Glutamic acid, N = 9.56% ($C_5H_9O_4N$ requires N = 9.50%), m.p. 209–210°C. $[\alpha]_D^{20} = +31.5°$ (hydrochloride).

Apparatus. Cell: a 250 c.c. cylindrical glass vessel, provided with a rubber stopper, carrying a condenser, a thermometer, and two elec-

(7) F. W. Foreman, *Biochem. J.*, **8** (1914), 481.

trodes. As for the divided cell, a rectangular glass jar (6.5×4.1×10 cm.) was used, which was bisected vertically, parchment paper being inserted at its joint and tightly braced from outside.

Anode (3×6 cm.) : platinum, carbon, or lead peroxide sheet.
Cathode (3×6 cm.) : lead or carbon sheet.
The distance between the electrodes was 1.7 cm.
Copper coulometer was used for the determination of amount of electricity.

Influence of Anode Material, Current Density and Diaphragm. The experiments were carried out under the following conditions.

(a) *Without a Diaphragm.*—About two grams of glutamic acid was dissolved in 200 c.c. of N.-sulphuric acid and electrolysed at room temperature in the above cylindrical cells which were connected in series. The nitrogen distribution in the solution are summarised in Tables I and II.

Table I.

Influence of Anode Material.

Anode/Cathode	Glutamic acid in gr.	Amp./dm².	Amp. hrs.	NH_3-N/Total N (%)
Pt/C	1.989	2.30	1.186	2.18
C/C	1.995	,,	,,	1.97
PbO_2/Pb	1.993	,,	,,	31.70

Table II.

Influence of Anode Material and Current Density.
(NH_2-N was determined by van Slyke's method)

Anode/Cathode	Glutamic acid in gr.	Amp./dm².	Amp. hrs.	NH_3-N/Total N (%)	NH_2-N/Total N (%)
Pt/C	2.001	1.89	2.648	3.90	94.7
C/C	2.000	,,	,,	4.70	90.4
PbO_2/Pb	2.100	,,	,,	48.5	32.6
Pt/C	2.000	7.97	2.790	2.20	97.8
C/C	2.000	,,	,,	—	86.6
PbO_2/Pb	2.000	,,	,,	29.7	40.7

Above results clearly show that the best yield of ammonia is obtained in the case when lead peroxide anode was used with current density of 2 amp./dm^2.

(b) *With a Diaphragm.*—Anolyte: 70 c.c. of N.-sulphuric acid containing about 0.7 gr. of glutamic acid. Catholyte: 70 c.c. of N.-sulphuric acid. Anode (3×6 cm.): platinum, carbon, or lead peroxide sheet. Cathode (3×6 cm.): carbon or lead sheet. The results are given in Table III.

Table III.

Influence of Diaphragm.

Anode/Cath.	Glut. acid in gr.	Amp./dm^2.	Amp. hrs.	NH_3-N/Total N (%)			NH_2-N/Total N (%)		
				Anoly.	Cath.	Sum	Anoly.	Cath.	Sum
Pt/C	0.6984	1.86	0.977	2.2	1.5	3.7	88.6	10.2	98.8
C/C	0.6984	,,	,,	2.2	1.3	3.5	87.2	10.6	97.8
PbO_2/Pb	0.6987	,,	,,	40.8	6.1	46.9	23.8	6.3	30.1

The percentage of ammonia obtained in the cases tabulated in Table III are similar to those in Table II, that is to say, no remarkable difference is found between the results of divided and undivided cells.

(c) *Oxidation at a Lead Peroxide Anode.*—About 6 gr. of glutamic acid was dissolved in 160 c.c. of N.-sulphuric acid, and oxidised in undivided cells, with lead peroxide anode at different current densities varying from 2 amp./dm^2. to 13 amp./dm^2. The results are given in Table IV.

Table IV.

Oxidation at a Lead Peroxide Anode.

Glut. acid in gr.	Amp./dm^2.	Amp. hrs.	NH_3-N/Total N (%)	NH_2-N/Total N (%)	Temp.	Volts.
5.987	1.96	7.377	59.3	14.5	—	3.5
6.022	7 38	6.436	62.6*	17.0	35°	4.8
5.997	13.3	6.143	55.4	19.0	50°	6.3

* In Table II, the better current efficiency is secured in the case of 1.89 amp./dm^2. This contradiction may be due to the difference in concentration of glutamic acid. (The former, 1% solution; the present, 3.8%).

Referring merely to the formation of ammonia, the best result was secured in the case of 7.38 amp./dm^2. By taking the yield of other oxidation products into account, 2 amp./dm^2. was chosen throughout the series of these researches as the most suitable condition. The amount of total-N extremely exceeds the sum of ammonia-N and amino-N. The difference may be (at least partly) ascribed to the presence of succinamic acid.

Isolation of Oxidation Products. Fifty grams of glutamic acid was dissolved in 600 c.c. of N.-sulphuric acid. The solution was placed in two equal rectangular glass vessels connected in series, each of them provided with an ebonite lid carrying a condenser and a thermometer. The solution was electrolysed with a lead peroxide anode (5.6×7.4 cm.) and a lead cathode (5.6×7.4 cm.) under the following conditions: the distance between the anode and the cathode, 3 cm.; C.D., 2 amp./dm^2.; current quantities, 55.8 amp. hours; temperature, 25°C. After the electrolysis, the nitrogen distribution in the solution was determined.

Nitrogen Distribution.

Total-N	98.6%
Ammonia-N (MgO)	87.0
Ammonia-N (30% NaOH)	3.9
Amino-N (van Slyke)	6.2

The ammonia-N (MgO) was determined by distillation over magnesium hydroxide under reduced pressure, and an excess of 30% NaOH was added to the residue. To estimate ammonia-N (NaOH) it was distilled under ordinary pressure, and the distillate was received in N.-sulphuric acid. This nitrogen represents the amount of succinamic acid.

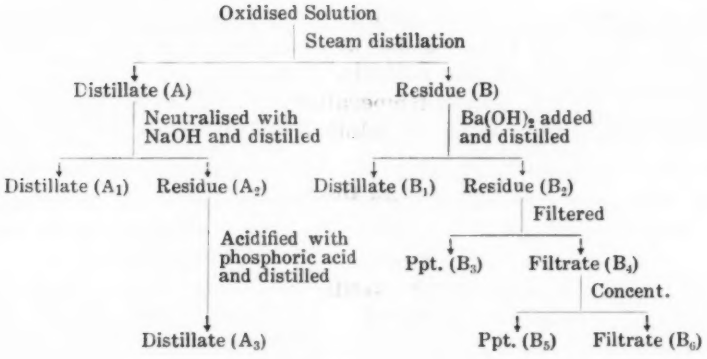
The oxidised solution was first submitted to steam distillation, the distillate (A) was neutralised with sodium hydroxide and redistilled. The first portion of the distillate (A_1) gave no iodoform reaction, and reduced neither Fehling's solution nor Tollens' reagent, but it gave only faint red colouration with fuchsin reagent. The original solution also showed no aldehyde reaction.

Volatile Acid.—Acetic Acid. The neutralised residue (A_2) was evaporated to dryness, an excess of syrupy phosphoric acid added, and it was redistilled. The volatile acid, obtained from the distillate (A_3), was identified as acetic acid by both ferric chloride and acetic ether reactions, and by its silver salt.

Anal.: Subst. = 0.2352; Ag = 0.1521 gr. Found: Ag = 64.66%.
Calc. for $C_2H_3O_2Ag$ (silver acetate): Ag = 64.64%.

The Volatile Base.—Ammonia. After making the residue (B) alkaline with barium hydroxide, it was submitted to distillation under reduced pressure, and a large quantity of ammonia was received in dilute hydrochloric acid (B_1). The ammonium chloride (8 gr.) thus obtained was identified as its platinic double chloride. Other bases were not present.

Anal: Subst. = 0.0983; Pt = 0.0432 gr. Found: Pt = 43.94%.
Calc. for $(NH_4)_2PtCl_6$ (ammonium chloroplatinate): Pt = 43.96%.



Succinic Acid.—The residue (B_2) was filtered. The precipitate (B_3), consisting of barium hydroxide, barium sulphate and organic salts of barium, was treated with sulphuric acid to remove barium, and from the concentrated filtrate free succinic acid crystallised out. The filtrate (B_4) was concentrated and barium succinate (B_5) was obtained which was then converted into free acid as usual. The joined yield was 18 gr. from 50 gr. of glutamic acid. It melted at 183°C. and the melting point showed no lowering when mixed with pure succinic acid.

Anal.: Subst. = 0.1437 gr.; Required N./10-NaOH = 24.27 c.c.
Calc. for $C_4H_6O_4$ (succinic acid): N./10-NaOH = 24.33 c.c.
Subst. = 0.1010; CO_2 = 0.1502, H_2O = 0.0464 gr.
Found: C = 40.56; H = 5.14%.
Calc. for $C_4H_6O_2$ (succinic acid): C = 40.63; H = 5.12%.

The mother liquor (B_6) of barium succinate, free from barium and sulphuric acid, was concentrated when it yielded glutamic acid, its hydrochloride decomposing at 205–206°C.

Succinamic Acid.—Fifty grams of glutamic acid was dissolved in 560 c.c. of N.-sulphuric acid and oxidised until one-half of the glutamic acid has been oxidised, the conditions being similar to those in previous cases of oxidation. The current applied amounted to 30.5 amp. hours.

The nitrogen distribution in the oxidised solution was as follows:—

Nitrogen Distribution.

Total-N	97.1%
Ammonia-N (MgO)	43.4
Ammonia-N (NaOH)	9.5
Amino-N (van Slyke)	44.0

The solution was made up to 1000 c.c. by adding water, and to isolate succinamic acid, half of the solution was neutralised with barium carbonate and barium hydroxide. The precipitate thus formed was filtered. The filtrate was concentrated to about 30 c.c. under reduced pressure at 50°C. and barium succinate formed was filtered. The filtered solution was treated with sulphuric acid to remove barium, and an excess of calcium hydroxide was added. Ammonia was driven off by distillation under reduced pressure and glutamic acid was recovered as its calcium salt.

After removing calcium as oxalate, the filtrate was concentrated to a syrup. The syrup was extracted with acetone. The crystals, formed after removal of acetone from the extract, was treated with ether to remove succinic acid, and it was recrystallised from acetone in colourless plate (0.7 gr.), m.p. 154–155°C. It was identified as succinamic acid[8], by the determination of nitrogen, mixed melting point test and conversion into silver salt.

Anal.: Subst. = 0.1253 gr.; NH_3 = 10.65 c.c. of N./10-H_2SO_4.
Found: N = 11.91%.
Calc. for $C_4H_7O_3N$ (succinamic acid): N = 11.96%.
Anal.: Subst. = 0.0498; Ag = 0.0239 gr. Found: Ag = 48.0%.
Calc. for $C_4H_6O_3NAg$ (silver succinamate): Ag = 48.18%.

Electrolytic Oxidation of Succinic Acid.—Separation of Acetic Acid. A solution of 20 gr. of succinic acid in 500 c.c. of N.-sulphuric acid was electrolysed with a lead peroxide anode and a lead cathode under the following conditions: anodic current density 2 amp./dm^2., temperature 25°C., current quantity 20.0 amp. hours. The oxidised solution was submitted to steam distillation. The distillate gave neither aldehyde nor

(8) *Ann.*, **134** (1865), 136; **162** (1872), 174.

ketone reactions. It was converted into sodium salt, dried, treated with phosphoric acid and distilled. Acetic acid was obtained from the distillate. It was identified as its silver salt.

Anal.: Subst. = 0.1359; Ag = 0.0877 gr. Found: Ag = 64.55%.
Calc. for $C_2H_3O_2Ag$ (silver acetate): Ag = 64.64%.

In conclusion, the author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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ON THE COPPER AGE IN ANCIENT CHINA. II.
(ON THE TRANSITIONAL PERIOD BETWEEN THE COPPER AND BRONZE AGE IN ANCIENT CHINA.)

By Tsurumatsu DŌNO

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In the previous paper, the present author reported[1] the results of chemical analyses of some metallic spear-heads of ancient China, which were made of almost pure copper. These specimens studied possess very primitive appearances and seem to belong to extremely antique species closely resembling to those relics unearthed from Yin Site in Honan. By this chemical investigation, the existence of the pure copper implements in ancient China being first confirmed, the author came to the conclusion that the real presence of the copper age in China preceding probably to the well known bronze age must be considered.

Encouraged by this discovery, the author has hereafter endeavoured to search for the specimens of the same kind as those recently analysed, in order to extend his study in this side. Fortunately several halberds in the type of those unearthed in Yin Site were put at his disposal by Mr. Sugimura in Peping, to whose kindness the author is very much indebted (compare Figs. I, II and III). According to the chemical study of these new specimens by the author, it was proved that one (A) of these three halberds contains so insignificant amount of tin that the arc spectral analysis was only able to detect the presence of this metal as several very

(1) Dōno, this Bulletin, **7** (1932), 347.

Fig. 1. Specimen A

Fig. 2. Specimen B

Fig. 3. Specimen C

faint lines, and consequently this specimen must be called the pure copper implement. The second one (B) involves tin in the amount detectable by an ordinary chemical analysis, namely about 0.60%[2]: even this, however, it must be classified in the copper implement from its very low contents in tin compared with ordinary bronze. As for the last specimen (C), it showed indeed a considerably high contents of tin (Sn = 2.19%) and it will undoubtedly be called a bronze implement in spite of that this is in the same type with the other two.

From the latter interesting fact, it may easily be concluded that the specimen (C) should have been manufactured in the transitional period between the copper and bronze age, and further that the copper age in ancient China existed very probably closely before the bronze age. It may also be supposed that the bronze age in ancient China should have begun at the time in which these types of halberds were made use of.

Experimental Part.

The chemical analysis as well as the metallographical study were carried out in the usual way[3] and the constituents, which are scarcely detected by the chemical methods, were found from their so called "raies ultimes" of the arc spectra. The results are given below.

(2) This low contents in tin must not be considered that this metal was added artificially.

(3) T. Dōno, *J. Chem. Soc. Japan*, **51** (1930) 463; **53** (1932), 100.

Wave-length of tin-lines	Specimen A	Specimen B	Specimen C
3175.16	doubtful	intense	intense
3262.50	,,	,,	,,

Results of chemical analyses	Specimen A	Specimen B	Specimen C
Sample (gr)	0.4890	0.5016	0.5085
Copper (%)	77.20	97.60	88.85
Tin (%)	Trace	0.60	2.19
Lead (%)	15.08	0.58	5.85
Iron (%)	2 80	0.08	0.08
Arsenic (%)	—	—	Trace
Nickel (%)	0.03	0.04	—
Gold (%)	Trace	Trace	Trace
Silver (%)	0.04	0.03	0.06
Total (%)	95.15	98.93	97.03

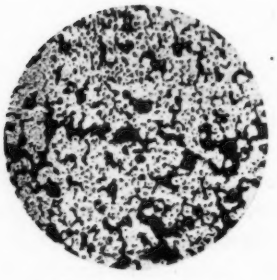

Fig. 4. Specimen A

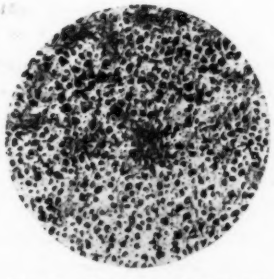

Fig. 5. Specimen A (etched)

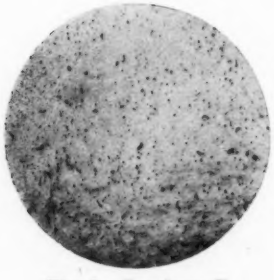

Fig. 6. Specimen B

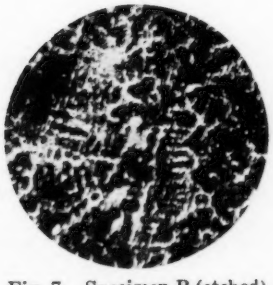

Fig. 7. Specimen B (etched)

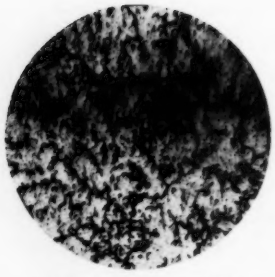

Fig. 8. Specimen C

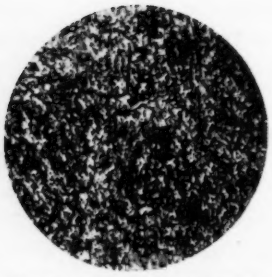

Fig. 9. Specimen C (etched)

As will be seen in the analytical results given above, the total values do not attain to 100%; this is, as was stated in the previous paper, due to oxygen which combined probably with metals during and after the manufacture of these weapons. As for the meaning of the existence of other metals was also already explained in the preceding paper.

Thus the author could add two more examples of pure copper implements in the ancient Chinese relics and was able to strengthen the recognition of the existence of the copper age in ancient China. The fact, that one of specimens now studied was of bronze, tells us that the beginning of the bronze age may be considered to have occurred at the time in which these types of halberds were made use of.

In conclusion, the author expresses his sincere gratitude to Prof. Dr. Shibata, Prof. Dr. S. Katō and Prof. Dr. K. Kimura for their kind guidances, and to Prof. Dr. Y. Harada, Dr. Y. Komai and Dr. N. Egami in the Archaeological Institute of the Faculty of Literature of Tokyo Imperial University, who gave valuable advices to his investigation from the standpoint of Archaeology and also to Prof. Dr. T. Mishima for the trouble of taking the metallographical photographs.

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